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Phonon density of states of iron from molecular dynamics simulations

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The phonon density of states (DOS) of bulk and surface iron was calculated using molecular dynamics simulations based on a recently constructed embedded atom potential. This potential showed a good agreement with experimental and first-principles data for both the fitted and predicted properties of BCC and FCC structures. For bulk Fe we have computed the DOS for both the BCC and FCC structure. Our results are compared to experimental data available in the literature and satisfactory agreements are obtained. Furthermore, we have evaluated the surface and adatom phonon DOS. The impact of the surface on the phonon DOS of nanocrystalline iron is briefly discussed.

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1. Introduction

Iron has always been the subject of extensive experimental, as well as theoretical investigations, because of its importance for many industrial applications and its abundance in the earth's core. The phase diagram of iron is very rich and it can be found in many crystallographic structures depending on the temperature and the pressure (see [1] and references therein).

It is known that empirical and semi-empirical interatomic potentials play a key role in any computer simulation in condensed matter and materials science [2]. They are designed to take into account the electronic density via many-body interaction terms. Among several many-body potentials one of the most popular is the, so called, embedded-atom method (EAM) potential [3]. Despite its simple form, in many cases this model provides a good description of the physical behaviour of metallic systems. EAM potentials are fitted to experimental data with no or little input from first-principles calculations. The recent trend, however, is to increase the amount of first-principles data in the fitting database and limit the experimental input, see e.g. [4] for a recent review.

Recently [5], the above approach has been applied to model the interaction in iron with parameters taken from fits to both experimental and first-principles data relevant to BCC and FCC structures. Note that, although the description of central forces underlying the EAM is not very accurate for BCC transition metals due the presence of a covalent component of bonding, the proposed model is apt to capture most of bulk and surface properties of both BCC and FCC structures. Furthermore, it accurately predicts the thermal expansion, phonon dispersion curves, mean-square displacements and surface relaxations of the metal. This potential can be useful in large scale and/or long simulation times for an adequate description of physical processes in iron, both in the β and the γ phases.

In this paper, our aim is to apply molecular dynamics (MD) simulations to compute the phonon density of states (DOS) of bulk BCC-Fe, as well as of FCC-Fe at room temperature. In addition, we will present our predictions for the phonon DOS of the (100) surface, as well as of an adatom vibrating on this surface. In Section 2 we present the computational methodology. Our results will be presented and discussed in Section 3. Finally our conclusions are drawn in Section 4.

2. Computational methodology

In the present work, we use an EAM potential, whose total energy for a monoatomic system can be represented as [3,4]

$$E_{tot} = \frac{1}{2}\sum_{ij} V(r_{ij}) + \sum_{i} F(\bar{\rho}_i), \qquad (1)$$

where $V(r_{ij})$ is the pair interaction energy between atoms i and j separated by a distance r_{ij} and F is the embedding energy of atom i as a function of the host electron density $\bar{\rho}_i$. The latter is given by

$$\bar{\rho}_i = \sum_{i \neq j} \rho(r_{ij}), \qquad (2)$$

where $\rho(r)$ is the electron density assigned to an atom. Thus, the EAM description of an elemental material requires three functions: $V(r)$, $\rho(r)$ and $F(\bar{\rho})$.

The potential was optimized by minimizing the weighted mean square deviation of selected properties of Fe from their target values corresponding to experimental and first-principles data. For further details about the fitting procedure the interested reader is addressed to [5].

We performed MD simulations in the canonical ensemble (NVT), using a system of 4500 atoms arranged on BCC or FCC lattices. The simulation boxes contained 20 layers with 225 atoms each, with periodic boundary conditions in all three directions. For the integration of the

equations of motion we used a time step of 5 fs and the Verlet algorithm. Thermodynamic averages were computed over 50 ps trajectories, after thermal equilibrium runs of 5 ps. The phonon DOS were obtained by Fourier transforming the velocity autocorrelation functions. Details of this computational procedure were reported elsewhere [6]. Surface phenomena were investigated by producing free surfaces. This is accomplished by fixing the computational box at a length twice as large as the thickness of the crystal along the direction normal to the surface; an infinite slab was thus constructed, delimited by two free surfaces. The above length is enough to avoid interactions between periodic slabs and, in addition the number of occupied layers is sufficient to reproduce bulk-like properties in its central part.

In [5], we have used this potential in conjunction with MD to compute several physical quantities. In particular, it has been used to investigate the self-diffusion of a Fe adatom on the Fe (100) BCC surface. Three main diffusion mechanisms were observed: hopping, diagonal exchange and non-diagonal exchange. It has been found that the diagonal exchange is the most favourable. In the next section, we will present our results for the phonon DOS for bulk BCC and FCC at room temperature, in addition to those obtained for the BCC-Fe(100) surface and the adatom on this surface.

3. Results and discussion

In Fig. 1, we report the phonon DOS of Fe-BCC at room temperature derived from the present MD simulations, along with the experimental one by using nuclear resonant inelastic scattering of synchrotron radiation [7]. To compare with the experimental data, we have multiplied our results by a normalization factor, so as to obtain equal areas for the two phonon densities. We note that our potential reproduces the three main peaks of the experimental DOS. The position of the high frequency peak is found to be in fair agreement with the experimental one, while the low energy peaks are located at lower frequencies than the experimental ones by about 1.4 THz.

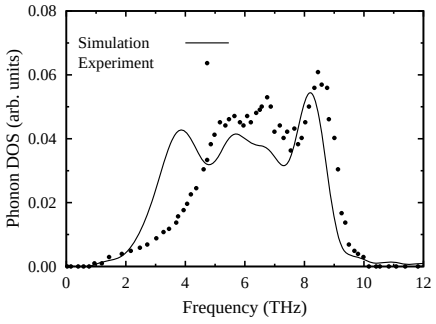

Fig. 1. Phonon DOS of Fe (BCC) derived from the MD simulations at 300 K in comparison with the measured DOS [7] by using nuclear resonant inelastic scattering of synchrotron radiation.

In Fig. 2 we show the DOS of Fe-FCC at room temperature in comparison with the corresponding experimental one, determined by means of nuclear resonant inelastic scattering of synchrotron radiation [7]. It is known that Fe-FCC is stable only in the range 1185 to 1667 K under normal atmospheric conditions. However, Fe precipitates larger than 30 nm in a Cu matrix are considered to be free from the influence of the host metal [7] and therefore their phonon DOS should be the same as that of the bulk Fe-FCC. In Fig. 2, the filled circles represent the experimental phonon DOS at room temperature for γ-Fe precipitates in Cu with a diameter equal to 80 nm. We note that the high frequency peak position of the DOS curve is correctly predicted by our EAM potential, but the computed low frequency peak is located at a lower frequency than that for Fe-FCC precipitates by about 1 THz. This discrepancy can be due to the instability of Fe-FCC at room temperature [7].

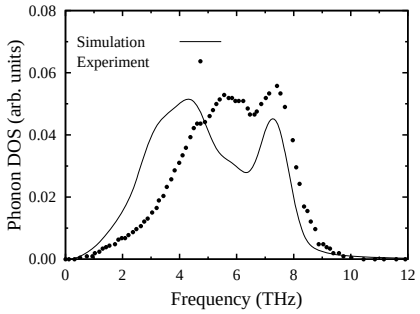

Fig. 2. Phonon DOS of Fe (FCC) computed by MD simulations at 300 K and the corresponding experimental points [7] determined by resonant inelastic scattering of synchrotron radiation.

In the following we will present some results related to the (100) surface of Fe-BCC. Let us recall that the surface relaxes to the opposite side relative to the middle of the sample as a function of the temperature. In Fig. 3 we show the phonon DOS of Fe(100) at room temperature, along the directions parallel and normal to the surface. From this figure, it is clear that the main peaks of the surface phonon DOS are located at lower energies than the corresponding bulk phonon peaks, which is compatible with the reduced number of interactions of surface atoms with neighbours.

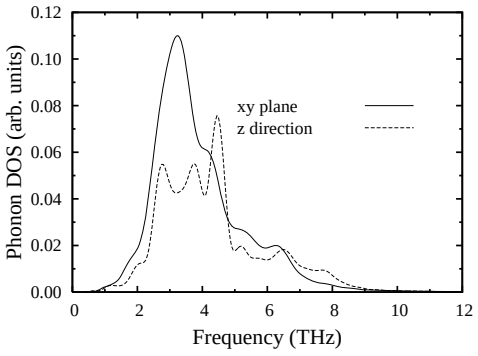

Fig. 3. Phonon DOS of Fe(100)-BCC at 300 K along the directions parallel and normal to the surface.

In Ref. [5], we have found that the adatom relaxes towards the surface. This might be related to a lowering of the adsorption energy upon heating the sample. In Fig. 4 we present the phonon DOS of a Fe adatom on the Fe(100) surface at room temperature along the directions parallel and normal to the surface. The vibrations of adatoms along these directions correspond to two well separated modes. The comparison of the spectra of adatoms with those for surface atoms (Fig. 3) shows firstly the presence of additional high energy peaks for the adatoms and secondly a shift of the surface modes towards lower frequencies.

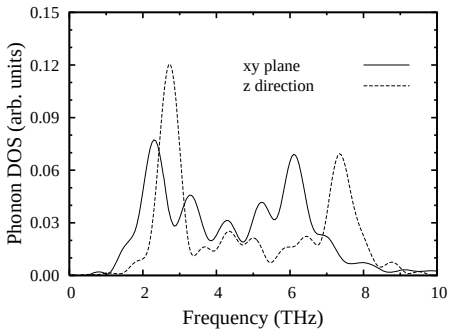

Fig. 4. Phonon DOS of a Fe adatom on Fe (100)-BCC surface at 300 K along the directions parallel and normal to the surface.

In [5] we have presented the calculated room temperature phonon dispersion. For the sake of completeness we will here reproduce the relevant comments. For BCC-Fe we found that the agreement between the MD simulations and experiment is quite good, except for the discrepancy found along the [110] direction for the transverse modes T_1 and T_2 in the vicinity of the N point, which is about 1.4 and 1.3 THz, respectively. A disagreement of about 0.5 THz was also found for the longitudinal mode close the H point and in the middle of the H and P directions. The discrepancy between our results and experiment in the phonon dispersion curves in BCC Fe is partly due to the fact that our potential was constructed to fit both BCC and FCC energies, unlike other EAM potentials that were fitted to describe the BCC lattice only. Of course, the angular-dependent potential of [8] removes most of the discrepancies at the expense of creating some limitations in the speed of the method for doing MD simulations.

For the computed phonon dispersion curves of FCC-Fe along high symmetry directions at 1428 K we noted that the longitudinal modes are generally well predicted, except for the zone boundary frequencies at the points X and L, where there is an overestimation of about 1 THz. On the other hand, there is a slight underestimation of the transverse modes, except the T_2 mode along the [100] direction in the vicinity of the point X.

In nanocrystalline materials, surface effects play an important role in comparison to their coarse grained counterpart. Indeed**,** the change in the behavior of these nanosized particles originates mainly from their large surface to volume ratio, while the major contributions to the physical and chemical properties originate mainly from their surfaces. It has been found that for nanocrystalline Fe there is an enhancement in the phonon DOS at low frequencies and an overall shift in the high frequency band beyond the top of bulk phonons [9]. In this respect we see that a combination of the calculated surface DOS together with the bulk ones is able to reproduce with a fair agreement the phonon DOS of nanocrystalline iron reported in [9].

4. Conclusions

We have investigated the phonon density of states of iron at room temperature, using a recently developed embedded atom method potential via molecular dynamics. The potential has proved its ability to reproduce the physical properties of both β and γ phases of iron. Here again we were able to check the ability of the potential to predict experimentally available data of the phonon DOS of the named phases. We have obtained an accurate description of the experimentally relevant peaks. Furthermore we have presented results for the surface phonon DOS**,** because of their relevance to nanocrystalline structures. We have obtained an enhancement of the low-frequency branch. Finally we have calculated the phonon DOS for an adatom vibrating on the (100) surface of Fe-BCC. In this case, the phonon DOS shows additional peaks in the high frequency branch compared to the surface phonon DOS. It would be interesting to extend this study to other BCC metals and to nanocrystalline structures.

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